CARBON COMPOSITION IN AN ENDANGERED MERIDIONAL PEAT BOG. RIBETEHILO LAGOON (DOÑANA NATIONAL PARK; SW-SPAIN)

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Introduction:
Sediment cores encompass information about past environmental changes, fire history and conditions of organic carbon deposition. The information provided is valuable for a range of research fields such as; global climate change, pollution assessment and control, etc. (González-Vila et al., 2003). During the last 30 years, a varied array of modern analytical techniques has been developed to assess the molecular composition of sedimentary organic carbon (OC) (Rothwell and Rack, 2006). In this work the modification in the down-core molecular composition of a 85 cm peat bog from the Ribetehilo lagoon (Doñana National Park; SW-Spain 37° 7'30.81"N; 6°37'50.19"O) is studied. In less than 50 years, the area occupied by peat bogs in the Gulf of Cádiz has been reduced drastically by more than 90% (Sousa and García Murillo, 1999). Therefore, this peat bog may well be considered as relict and one of the last and more Meridional still in existence. For this work, 5 samples taken at different depths were analysed in detail (0-10, 25-30, 45-50, 65-70 and 80-85 cm) using analytical pyrolysis (Py-GC/MS) and ultra-high resolution mass spectrometry (ESI-FT-ICR/MS), the latter one was used with humic extracts because solubility is required. The detected compounds were grouped into 6 main biogenic families; lipids, unspecific aromatic compounds, polyphenols, protein, carbohydrates and condensed compounds.

Results:
The pyrograms of the shallow layer (0-10 cm) showed that the organic carbon (OC) composition was dominated by carbohydrate and polyphenol compounds (40% and 20%, respectively), whereas down core the OC composition was gradually dominated by lipids and unidentified aromatic compounds (from 27.7% to 40.9%, and from 18.2% to 39.7%, respectively) (Fig. 1A). At the same time, a conspicuous depletion of labile compounds and a complete disappearance of polyphenol compounds in the deepest sub-sample, was observed. These results suggest that while shallow OC reflects the molecular signature of a more or less fresh material, OC in deeper bog samples underwent higher chemical alteration produced by either higher microbial activity or chemical transformations also occurring in an anoxic environment. The latter is supported by a lower soil conductivity and basic pH values (~10 μScm^{-1} and ~8, respectively) as well as light C isotopic composition ($\delta^{13}C$ < -29‰ VPDB) found at depth. In addition, an enrichment of condensed organic compounds is observed from the middle of the core sample to the bottom layer. This may be due either to the existence of older wildfires or to a transport of highly humification OC from upper layers.

More than 8700 unique formulas were detected by ultra-high resolution mass spectrometry of alkaline extracts of the peat. Van Krevelen diagrams for more than 2500 chemical compounds, made up of only C, H and O-containing formulas, are depicted in Fig. 1B & 1C. For the shallow sample the OC composition is dominated (larger bubble size) by oxidized compounds (carbohydrate and polyphenols) and almost negligible contribution of hydrogen-rich compounds (lipids and proteins) is found. In addition, this sample displayed a relatively high amount of condensed compounds not observed by Py-GC/MS. Bottom OC composition (Fig. 1C) was characterized by a lower chemical diversity of total compounds (4125 vs, 6374 in shallow sample) and C, H, O compounds (1883 vs 2317 in shallow sample) and a relatively high contribution of recalcitrant compounds with a lower O/C value and a conspicuous contribution of microbial compounds with high H/C ratio (proteins and lipids). In addition, this bottom sample (80-85 cm) showed a conspicuous contribution of condensed aromatic compounds.

Conclusions:

The results obtained by the two techniques were found similar, showing as shallow OC composition was dominated by fresh material from upper vegetation cover, while more transformed and humified material was accumulated in the bottom layers. This may be due to i) intense microbial activity combined with large fluctuations of the water front occurring during the year; and/or ii) anaerobic processes. In general, this lack of peat preservation at depth is probably a sign of bog degradation processes, probably linked with climate changes to which Mediterranean wetlands are especially responsive to such a perturbation.

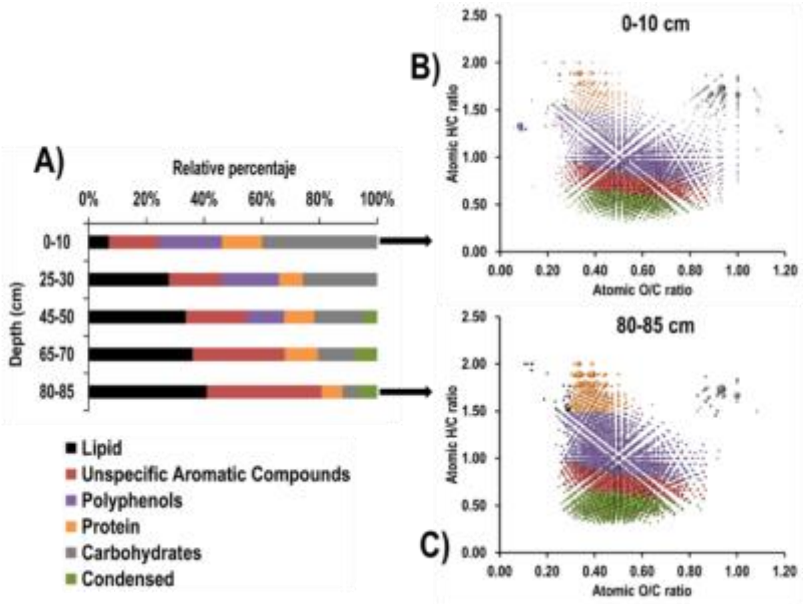

Figure 1. A) *Relative percentage of the main chemical families identified by Py-GC/MS along a 85 cm peat layer;* ***B)*** *and* ***C)*** *van Krevelen diagrams of CHO compounds of shallow (0-10 cm) and bottom sample (80-85 cm), respectively. Bubble size represents the relative intensity of each compounds. Chemical families are represented by a differentiated color.*

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Acknowledgements:

The authors thanks the Spanish Ministry of Economy and Competitiveness (MINECO) through the INTERCARBON project (CGL2016-78937-R). N.T. Jiménez-Morillo thanks the MINECO for funding his FPI research grants (BES-2013-062573). We thank COSMIC for the use of FTICRMS instrument and Derek Waggoner for assistance in obtaining and preparing the FTICR-MS data.